The Absolute Configuration of d-Tartaric Acid

Jürg Waser

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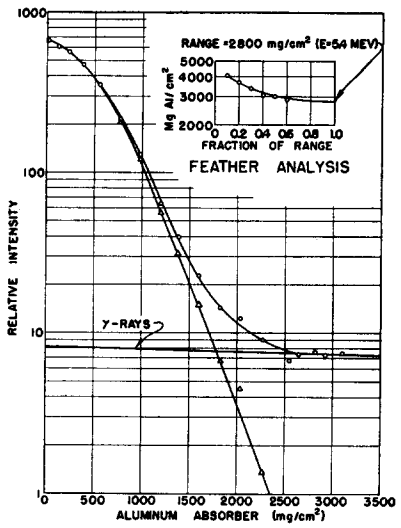


FIG. 2. Beta-absorption curve.

LaF_3 twice. Then after allowing 1.5 minutes for more Y^{94} to grow in from its 2-min. Sr parent, yttrium was isolated from the solution.

From eleven beta-decay curves (Fig. 1) and four gamma-decay curves the average value of the half-life was determined as 16.5 ± 1.0 minutes. The decay curves showed two major components: 16.5-min. Y and 10-hr. Y. In most cases a very small amount of an intermediate component appeared also, probably 3.5-hr. Y. The latter introduced some uncertainty into the resolution of the decay curves. By irradiating for no more than 10 minutes and by doing the analyses within a few minutes after the irradiations, the amount of 3.5-hr. Y which grew from its 2.7-hr. Sr parent was kept very low. However, it could not be eliminated entirely. The decay curves published by Hahn and Strassmann[1] show the 3.5-hr. component in considerably higher relative intensity. This may be an indication of rare earth contamination since a 3.7-hr. La is known. The greater value of 20 minutes they report for the half-life of Y^{94} may have been caused by contamination with 19-min. La and other rare earth isotopes.

The γ-ray intensity seemed to decay with a slightly shorter half-life (15.5 min.) than the β-ray intensity (16.7 min.)

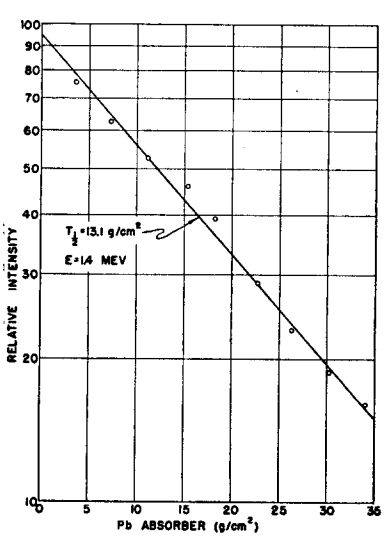


FIG. 3. Gamma-absorption curve.

Although the difference was within experimental error, the possibility of the existence of two Y isotopes with similar half-lives and radiations was considered. This appears improbable because the half-lives obtained were the same whether the samples were isolated directly from fission recoils or from the strontium parent(s). The assumption of two Y isotopes would imply that their half-lives are almost identical and/or that both have strontium parents of approximately equal half-lives. Either situation is unlikely.

The beta- and gamma-radiations were investigated by following the decay of several samples through a series of Al and Pb absorbers using a mica window (3 mg/cm²) Geiger-Mueller counter. From the resolved decay curves the absorption curves shown in Figs. 2 and 3 were constructed. The Feather analysis of the aluminum absorption curve indicates a range for the beta-rays of 2800 mg Al/cm², corresponding to a maximum energy of 5.4 Mev. The half-thickness in lead for the gamma-rays is 13.1 g/cm², corresponding to an energy of 1.4 Mev. The Y samples used for the γ-ray absorption curve were isolated directly from an irradiated uranyl nitrate solution. Standard rare earth separations were used only in this case. It was found that six potassium rare earth double sulfate precipitations were needed in order to remove rare earths sufficiently. Praseodymium and neodymium carriers were added as well as lanthanum.

* This document is based on work performed at Los Alamos Scientific Laboratory of the University of California under Government Contract W-7405-eng-36.

** Now at Brookhaven National Laboratory, Upton, Long Island, New York.

[1] O. Hahn and F. Strassmann, Zeits. f. Physik **121**, 729 (1943).
[2] Katcoff, Miskel, and Stanley, Report LA-659 (Feb. 1948).

The Absolute Configuration of *d*-Tartaric Acid

JÜRG WASER
The Rice Institute, Houston, Texas
March 11, 1949

IT is well known that the usual x-ray data alone do not permit a distinction between the two possible enantiomorphic structures of an optically active crystal. It seems to have escaped general notice, however, that in favorable cases such an assignment may be made if the face development of the crystal is taken into consideration.

The crystal structure of *d*-tartaric acid published recently by Beevers and Stern[1] makes possible an absolute determination of the structural configuration of the *d*-tartaric acid molecule. This is all the more important, as an assignment of absolute configuration to a molecule related to tartaric acid and therefore to a whole class of optically active molecules on the basis of a physical theory of optical activity,[2] seems to be open to criticism.[3]

Figure 1 represents a projection onto the (100) plane of the structure of *d*-tartaric acid as determined by Beevers and Stern.[1] The *a* axis is oriented towards the reader, the *b* axis to the right, and the *c* axis up (although the possibility is left open by Beevers and Stern[1] that the *b* axis might point to the left). The van der Waals radii of carbon and oxygen were chosen to be 1.4A and 1.6A, respectively, and the hydrogen atoms were omitted. The molecules drawn with heavy lines lie above the others to which they are related by twofold screw axes in the *b* direction. A molecule in the upper left shows in detail the relationship between the carbons and oxygens except for one concealed carboxyl oxygen. Figure 2 shows the habits of the monoclinic hemihedral crystals of dextro-rotatory ($d+$) and of levo-rotatory ($l-$) tartaric acid. The monoclinic angle between the faces (100) and (001) is 100° 17′ in either crystal. The orientation of the *b* axis is the same in the two figures.

The important distinguishing feature is seen to be the appearance of the right sphenoid (011) (faces (011) and (01$\bar{1}$)) on dextro-rotatory tartaric acid and of the corresponding left sphenoid on levo-rotatory tartaric acid. It is apparent that the structure of Fig. 1 corresponds to the face development of the dextro-rotatory tartaric acid crystal. A molecular arrangement as drawn would tend to develop the faces (011) and (01$\bar{1}$) whose traces are shown in Fig. 1. The rate of growth perpendicular to these faces would be low, due to the unfavorable orientation of the molecules. For instance, a molecule approaching from the right a completed layer bounded by the plane (011) (Fig. 1) would have to be oriented properly within a narrow margin to be able to form the one or two hydrogen bonds that will hold it in position. Furthermore, only this one, or these two, hydrogen bonds will keep the molecule from breaking loose again before further supporting molecules have been captured in its neighborhood by the surface. The resulting low rate of crystal growth normal to (011) will cause the face (011) to develop very prominently. The non-appearance of the faces (0$\bar{1}$1) and (0$\bar{1}\bar{1}$) is, on the other hand, due to rapid crystal growth normal to the corresponding planes. Let, for instance, a crystal be bounded by the layer of molecules to the right of the trace of (011) in Fig. 1 (this trace

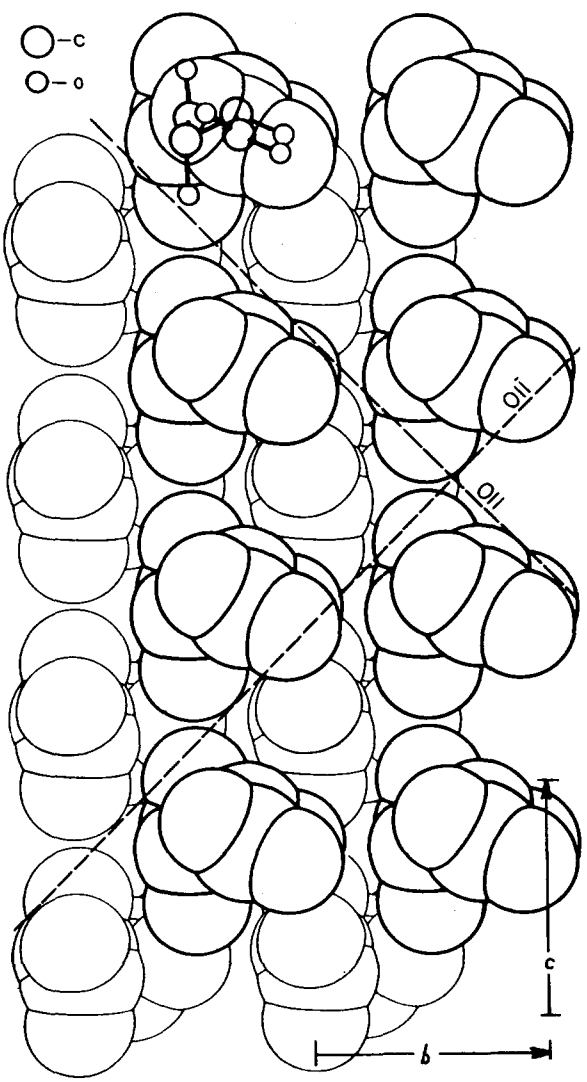
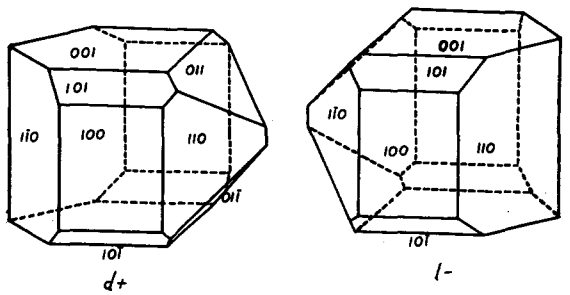


FIG. 1.



TARTARIC ACID

FIG. 2.

would thus actually correspond to the face (0$\bar{1}\bar{1}$)). A molecule approaching from the left would eventually be bonded to the surface by three or four hydrogen bonds and would be captured and swing into position from a much wider range or orientation than was the case for the (011) face. The face (1$\bar{1}$0), can also be visualized in Fig. 1. It intersects the figure plane parallel to the c axis, for instance along the left-hand margin of the figure, and slants down from the right to the left.

The absolute configuration of dextro-rotatory tartaric acid is therefore that given by the molecule in the upper left corner of Fig. 1 or, if represented by the projection formula,[4]

$$\begin{array}{l} {}^{1}\mathrm{COOH} \\ | \\ \mathrm{H}\text{—}{}^{2}\mathrm{C}\text{—}\mathrm{OH} \\ | \\ \mathrm{HO}\text{—}{}^{3}\mathrm{C}\text{—}\mathrm{H} \\ | \\ {}^{4}\mathrm{COOH}, \end{array}$$

by the provision that the hydroxyl groups and methylene hydrogens are to lie below the plane containing carbon atoms 2 and 3 and the carboxyl groups to lie above that plane. This is just the opposite configuration from the one assigned by E. Fischer[4] on a postulatory basis.

A determination of absolute configuration on the basis of the pyroelectric effect[5] would involve an assumption about the charge distribution in the molecule and require a knowledge of the position of the hydrogen atoms.

[1] C. A. Beevers and F. Stern, Nature **162**, 854 (1948).
[2] W. Kuhn, Zeits. f. physik. Chemie **B31**, 23 (1936); Naturwiss. **26**, 289 (1938); J. G. Kirkwood, J. Chem. Phys. **5**, 479 (1937); **7**, 139 (1939); Gorin, Walter, and Eyring, J. Chem. Phys. **6**, 824 (1938).
[3] E. Hückel, Zeits. f. Elektrochemie **50**, 13 (1944); W. Kuhn and R. Rometsch, Helv. Chim. acta **27**, 1346 (1944), p. 1363; R. Rometsch and W. Kuhn, *ibid.* **29**, 1483 (1946).
[4] See e.g., K. Freudenberg, *Stereochemie* (Leipzig und Wien, 1933), p. 662ff.
[5] See e.g., P. Groth, *Physikalische Krystallographie* (Leipzig, 1895), p. 353.

Thermodynamic Functions of CH_3SH and $(CH_3)_2S$

JOHN L. BINDER
Akron, Ohio
March 9, 1949

SOME time ago the writer had occasion to compute the thermodynamic functions of methyl mercaptan and dimethyl sulfide for use in equilibrium studies. In view of the present interest in sulfur compounds it seemed desirable to present the results of these calculations in an abbreviated form now for the use of others. A more complete discussion of the calculations will be published later.

The entropies, free energies, heat capacities, and heat contents were calculated for several temperatures by the usual statistical methods. The hindered rotation potentials,